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SOLVENT EFFECTS ON PHOTOPHYSICAL PARAMETERS FOR COUMARIN LASER --ETC(U)
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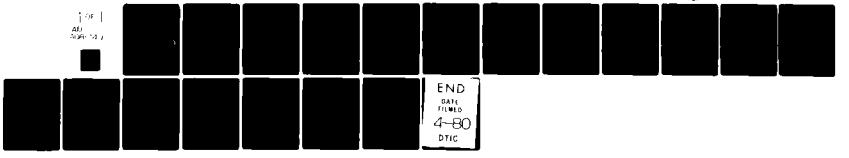

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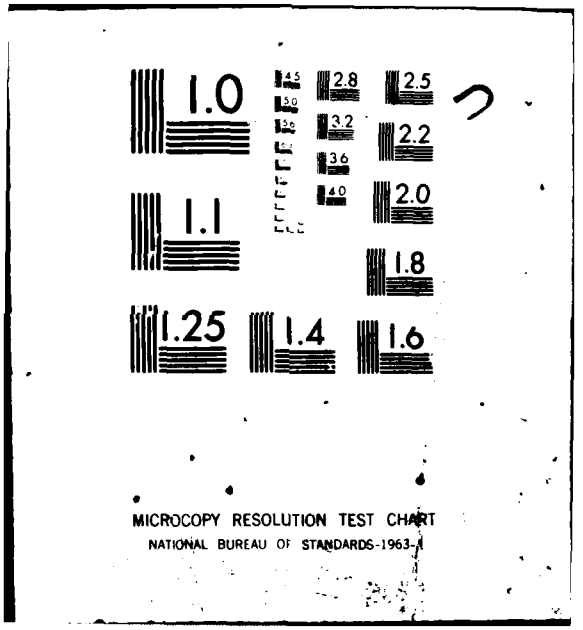
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Arthur M. Halpern

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The red shifts of absorption and emission bands of coumarin laser dyes were studied as a function of solvent polarity and hydrogen bonding. Spectra were correlated with solvent parameters, π^* and α, and those solvents resulting in the largest Stokes shifts of dye emission were identified. Solvent effects on emission yield and lifetime revealed a major non-radiative decay path for dyes in which the 7-amine function is free to adopt a non-planar conformation.

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TECHNICAL REPORT NO. 2

SOLVENT EFFECTS ON PHOTOPHYSICAL PARAMETERS FOR COUMARIN LASER DYES

by

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SOLVENT EFFECTS ON PHOTOPHYSICAL PARAMETERS FOR COUMARIN LASER DYES

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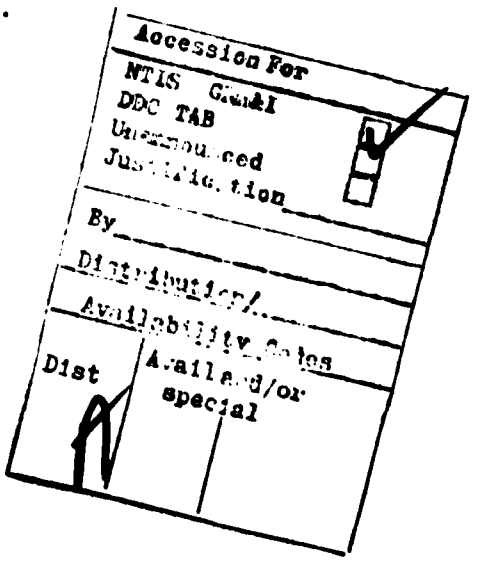
The red shifts of absorption bands of coumarin dyes in polar solvents correlate with the solvent polarity- polarizability parameter π^*. Emission frequencies correlate well with the hydrogen bonding parameter, α and show a regular dependence on π^* if a solvent polarizability correction term is incorporated for chlorinated hydrocarbon and aromatic solvents. Quantum yield and lifetime measurements reveal that the reduced emission observed for dyes with non-rigid structures is associated with enhanced nonradiative decay in polar solvents. The solvent effect on fluorescence yield is interpreted in terms of the intervention of planar and non-planar excited species which appears to be general for polar dyes.



The strong emission of aminocoumarin dyes derives from the polar character of low-lying excited states.[1] The Stokes shift and yield of fluorescence and the potential for lasing are influenced by the maintenance of a large excited state dipole moment. Dye substitution patterns and dye medium both play important roles in dipole stabilization. Recent studies[2] suggest that relatively subtle medium (solvent) effects may be exploited in optimizing the output of dye lasers which employ coumarin dyes. We have examined the influence of solvent on the photophysical properties of a number of coumarin dyes and find certain regular and predictable functions of solvent polarity which are reported herein. Particular attention has been paid to the fall off in fluorescence yield in polar solvents which has been observed for dyes with non-rigid structures.[1,3] We are able to assign this effect to a non-radiative decay path on the basis of emission yield and lifetime measurements and using a current model of polar excited state dynamics.

Dyes chosen for study are the fluorinated aminocoumarins shown below with number designations, C1F (35), C6F (153), and C8F as previously reported[1,5] (numbers in parenthesis refer to the Eastman Kodak system[3]). Absorption data for a variety of solvents are shown in Table 1. Measured extinction coefficients were in the range, ε = 15,000 - 20,000. The regular dependence of emission maxima on solvent polarity for non-hydrogen-bonding solvents was treated quantitatively using the solvent parameters π^*. This scale of solvent polarity has been developed by Kamlet and Taft[6] from absorption data for a number of aniline derivative indicator dyes and reflects solvent polarity-polarizability in the absence of specific interactions such as hydrogen bonding.

Correlations of absorption frequencies with π^* are shown in Figure 1. Linear least squares analysis of the data leads to the following equations describing the solvatochromic effect. (Correlation coefficients, r, are included).

For C1F, $\nu_a = 26.5 - 1.67\ \pi^*$ ($r = 0.942$) (1)

For C6F, $\nu_a = 25.4 - 1.89\ \pi^*$ ($r = 0.972$) (2)

For C8F, $\nu_a = 26.1 - 1.78\ \pi^*$ ($r = 0.977$) (3)

The intercepts of ν_a vs. π^* plots approximate the absorption frequency for the reference solvent cyclohexane ($\pi^* = 0$) and reflect the role of substituents in excited state dipole stabilization in the absence of any significant solvent dipole interaction. The greater excited state dipole stabilization for C6F over C1F is consistent with the introduction of electron donating alkyl groups at ring positions 6 and 8 for this series. The slopes of π^* plots reflect the strength of interaction of excited dye with solvent dipoles or induced dipoles, a susceptibility which is similar for the series.

Emission maxima and Stokes shift for the selected dyes (Table 2) were obtained from corrected fluorescence spectra recorded on a Perkin-Elmer MPF 44A spectrophotometer. Fluorescence quantum yields were obtained using quinine sulfate in 1.0 N H_2SO_4 ($\Phi = 0.55$) as the fluorescence standard with refractive index and differential absorption corrections. Emission lifetimes were determined using single photon counting apparatus and analytical deconvolution methods previously described.[7,8] The emission quantum yield and lifetime results are collected in Table 3.

The well-known shift of emission maximum to longer wavelength and a general broadening of the flourescence band on increase in solvent polarity[1] was reproduced in our study. The dependence on solvent polarity-polarizability was less regular, however, than that found for absorption measurements. Plots of υ_f and π^* for C1F and C8F, for example, revealed a trend but were not strictly linear as illustrated in Figures 2 and 3.

In contrast to the emission data for aprotic (non-hydrogen bonding) polar solvents, fluorescence maxima for C6F and C8F in alcohols were readily correlated with a single solvent property. As shown in Figure 4, a linear relation was obtained with the Kamlet/Taft[9] parameter, α, an empirically derived constant reflecting the ability of solvent to donate a hydrogen bond (implicating a specific dipole-dipole association with solute). Least squares analysis of the data provided the following expression relating fluorescence maxima and the hydrogen bonding parameter. (A less satisfactory correlation of ν_f, vs. α was obtained for the non-rigid dye.)

For C6F, $\nu_f = 21.09 - 2.61\,\alpha$ $(r = 0.978)$ (5)

For C8F, $\nu_f = 21.40 - 2.29\,\alpha$ $(r = 0.990)$ (6)

Solvatochromic equations reflecting red shifts of emission due to interaction with hydrogen bonding and non-hydrogen bonding solvents were obtained when the polarizabilities of different classes of aprotic solvents were taken into account. We noted that in the plots shown in Figures 2 and 3, the solvents responsible for most of the scatter were either aromatic (benzene, toluene) or chlorinated (tetrachloroethane). These classes of solvents with polarizabilities which exceed those of non-chlorinated aliphatic solvents have been shown to give deviant behavior in π^* correlations.[10] Thus, the following "all solvent" equation has been proposed[10,11] for regression analysis employing α, π^*, and a correction term for π^*, $d\,\delta$, a measure of enhanced polarizibility (δ = 0.5 for chlorinated solvents and 1.0 for aromatic solvents).

$$\nu_f = \nu_0 + s(\pi^* + d\,\delta) + a\,\alpha \qquad (7)$$

Least squares multiple regression analysis[11] of the fluorescence data for the fluorinated coumarins led to the following solvatochromic equations.

For C1F, $\upsilon_f = 22.8 - 3.50\ (\pi^* - 0.20\ \delta) + 1.42\ \alpha$ ($r = 0.981$) (8)

For C6F, $\upsilon_f = 21.9 - 3.28\ (\pi^* - 0.20\ \delta) + 1.52\ \alpha$ ($r = 0.990$) (9)

For C8F, $\upsilon_f = 22.3 - 3.32\ (\pi^* - 0.20\ \delta) + 1.20\ \alpha$ ($r = 0.975$) (10)

The best fit of parameters for the emission data was provided by setting the scaling factor for the polarizability correction term, d = - 0.20. This value is similar to that found (- 0.19) in an "all solvents" correlation of emission frequencies for a merocyanine dye similar to the coumarins, N,N-dimethyl-4(dichloro-1,3,5-tria zinyl)aniline.[11]

Equations 8 - 10 allow the dissection of solvent shifts of emission frequencies into relative influences of solvent polarity and hydrogen bonding.[f] The solvatochromic equations also provide a means for predicting emission maxima and Stokes shifts for a wide variety of solvents whose π^* and α parameters are known.[9-10] Notably, the largest Stokes shifts are predicted for non-chlorinated aliphatic solvents having high π^* values. Alcohols as a class provide large Stokes shifts as well, and among the alcohols differences in $\upsilon_a - \upsilon_f$ are relatively small.

Changes in emission yield and lifetime accompanied the shift of dye emission to longer wavelengths with increase in solvent polarity. Some reduction in fluorescence yield was noted for all three selected dyes (Table 3), but the effect was most striking for C1F. This phenomenon, already associated with dye substitution pattern in which the amine geometry at the 7-position is nonrigid[3], could in principle be the result of changes in either radiative or nonradiative decay parameters. These rate constants are readily calculated from fluorescence yield and lifetime data using the relationships: $k_f = \phi_f / \tau_f$ and $k_{nd} = 1 - \phi_f / \tau_f$. The results in Table 4 show that the sharp fall off in relative fluorescence intensity for C1F is in part due to a diminished rate of radiative decay (as with the other

dyes) but the more important effect is a large increase in non-radiative deactiviation. In fact a >200-fold range in k_{nd} for C1F contrasts with a <10-fold change for C6F and C8F.

The notion that a radiationless decay involving motion of the amine substituent for C1F is supported by other medium effect data. In the very polar (ϵ = 42.5) yet highly viscous (μ = 945 cP) solvent glycerol, C6F and C8F emission yields and lifetimes were further reduced (i.e., the trend for the very polar solvents continues) yet the effect on C1F was to restore emission parameters to values which are similar to those found for the rigid dyes.

We interpret the principle effect of solvent medium on fluorescence yield and lifetime for the coumarins in terms of a rotation dependent radiationless decay, an internal conversion of the emissive state to a twisted conformation which is relatively non-emissive. Thus, excitation leads to a polar, planar excited state of the dye which is moderately stabilized by interaction with solvent and which gives rise to most if not all observed fluorescence. This intramolecular charge-transfer or ICT state is nominally represented by a polar resonance structure, (see below), a form which is more important in the excited state than in the ground state. In very polar media and where structure permits the ICT state relaxes further to a fully charged (zwitterionic) excited species having a non-planar geometry (a TICT or twisted intramolecular charge transfer state). The model is adopted from the current proposal of Grabowski, Cowley, and Baumann[13] concerning the behavior of a variety of polar excited species.

Photophysical parameters for other dyes (e.g., C1 having a "free" $-N(C_2H_5)_2$ group and C102, similar in structure to C6F)

have been measured in our laboratories with results consistent with the ICT - TICT model. However, within the family of coumarins there may be two exceptional groups of compounds. Dyes with an unsubstituted $-NH_2$ substituent group such as C120[14] and C151[15] as well as coumarins substituted with the benzothiazole group (C7 and C30)[14] do not show significantly reduced emission yields and lifetimes in the most polar solvents. Differences in NH_2 - vs. NR_2 substituted dyes are consistent with recent calculations[16] on excited state rotational relaxation in substituted benzonitrile and related systems.

In summary, solvent effects on the position, intensity, and lifetime of emission of a group of representative coumarin dyes have been measured. Reduced emission yields in polar solvents, reminiscent of the behavior of rhodamine dyes,[1] and related effects of dye structure (rigid vs planar chromophore geometry) and dye solvent properties (polarity and viscosity) have been observed. Regular dependences of absorption and emission maxima on solvent polarity-polarizability and hydrogen bonding properties have been identified, providing some means for "solvent tuning" of emission bands.

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FOOTNOTE

*Solvent effects other than solvent polarity and hydrogen bonding have been considered. Coumarin emission frequencies for alcohol solvents have been correlated with the Hilde brand δ parameter reflecting solvent cohesion.[12]

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Table 1. Absorption Maxima for Courmarin Dyes as a Function of Solvent[a]

Solvent $(\pi^*)(\alpha)$[b]	C1F		C6F		C8F	
	λ_a	ν_a	λ_a	ν_a	λ_a	ν_a
cyclohexane (0.0)	376	26.6	393	25.5	382	26.2
ethyl ether (0.27)	387	25.8	405	24.7	393	25.5
p-xylene (0.43)	390	25.6	405	24.7	295	25.3
ethyl acetate (0.55)	392	25.5	409	24.5	398	25.1
tetrahydrofuran (0.58)	394	25.4	413	24.2	401	24.9
benzene (0.59)	387	25.8	410	24.4	397	25.2
acetone (0.68)	396	25.3	416	24.0	404	24.8
acetonitrile (0.76)	396	25.3	418	23.9	405	24.7
tetrachlorethane (0.95)	404	24.8	422	23.7	409	24.5
t-butyl alcohol (0.46)(0.62)	397	25.2	416	24.0	404	24.8
i-propyl alcohol (0.74)(0.75)	400	25.0	420	23.8	407	24.6
n-butyl alcohol (0.46)(0.79)	400	25.0	420	23.8	408	24.5
n-propyl alcohol (0.53)(0.81)	401	24.9	421	23.8	409	24.5
ethanol (0.54)(0.85)	400	25.0	421	23.8	408	24.5
methanol (0.60)(0.99)	401	24.9	422	23.7	409	24.5
glycerol (0.73)(0.98)[c]	413	24.4	434	23.0	420	23.8
ethanol-water (50:50)	412	24.3	435	23.0	421	23.8

[a] λ_a in nm; ν_a in kK.

[b] Solvent parameters in parenthesis.

[c] Parameters for ethylene glycol.

Table 2. Fluorescence Emission Maxima for Coumarin Dyes[a]

Solvent	C1F			C6F			C8F		
	λ_f	ν_f	$\nu_a-\nu_f$	λ_f	ν_f	$\nu_a-\nu_f$	λ_f	ν_f	$\nu_a-\nu_f$
cyclohexane	433	23.1	3.51	455	22.0	3.47	439	22.8	3.40
ethyl ether	458	21.8	4.01	475	21.1	3.64	475	21.1	4.40
p-xylene	458	21.8	3.85	475	21.1	3.64	475	21.1	4.27
ethyl acetate	479	20.9	4.63	501	20.0	4.45	489	20.5	4.68
tetrahydrofuran	479	20.9	4.50	500	20.0	4.21	489	20.5	4.41
benzene	465	21.5	4.36	476	21.0	3.39	474	21.1	4.09
acetone	500	20.0	5.25	515	19.4	4.69	504	19.8	4.91
acetonitrile	501	20.0	5.30	522	19.2	4.73	510	19.6	5.08
tetrachloroethane	475	21.1	3.70	500	20.0	3.74	484	20.7	3.79
t-butyl alcohol	505	19.8	5.40	513	19.5	4.55	499	20.0	4.71
i-propyl alcohol	500	20.0	5.00	522	19.2	4.65	509	19.7	4.92
n-butyl alcohol	497	20.1	4.88	527	19.0	4.83	511	19.6	4.94
n-propyl alcohol	507	19.7	5.21	528	18.9	4.81	512	19.5	4.92
ethanol	509	19.7	5.35	531	18.8	4.92	515	19.4	5.09
methanol	515	19.4	5.51	537	18.6	4.38	520	19.2	5.22
glycerol	524	19.1	5.13	546	18.3	4.72	530	18.9	4.94
ethanol-water (50:50)	523	19.1	5.15	542	18.5	4.55	529	18.9	4.85

[a] λ_f in nm; ν's in kK.

Table 3. Dye Fluorescence Quantum Yields and Lifetime (ns)

Solvent	C1F		C6F		C8F	
	Φ_f	τ_f	Φ_f	τ_f	Φ_f	τ_f
cyclohexane	1.04	4.1	0.73	4.3	0.93	4.2
ethyl acetate	0.64	4.6	0.88	5.4	0.72	
acetonitrile	0.09	0.60	0.43	5.6	0.68	5.6
ethanol	0.09	0.85	0.26	3.4	0.65	5.1
ethanol-water	0.03	0.45	0.26	4.7	0.43	4.5
glycerol	0.14	2.7	0.17	3.5	0.27	

Table 4. Radiative and Non-radiative Decay Parameters[a]

Solvent	C1f		C6F		C8F	
	k_f	k_{nd}	k_f	k_{nd}	k_f	k_{nd}
cyclohexane	2.4	<0.10	1.7	.63	2.2	.17
ethyl acetate	1.4	0.78	1.6	.22		
acetonitrile	1.5	15.	.77	1.0	1.2	.57
ethanol	1.1	11.	.77	2.2	1.3	.69
ethanol-water	0.67	22.	.55	1.6	.96	1.3
glycerol	0.52	3.2	.49	2.4		

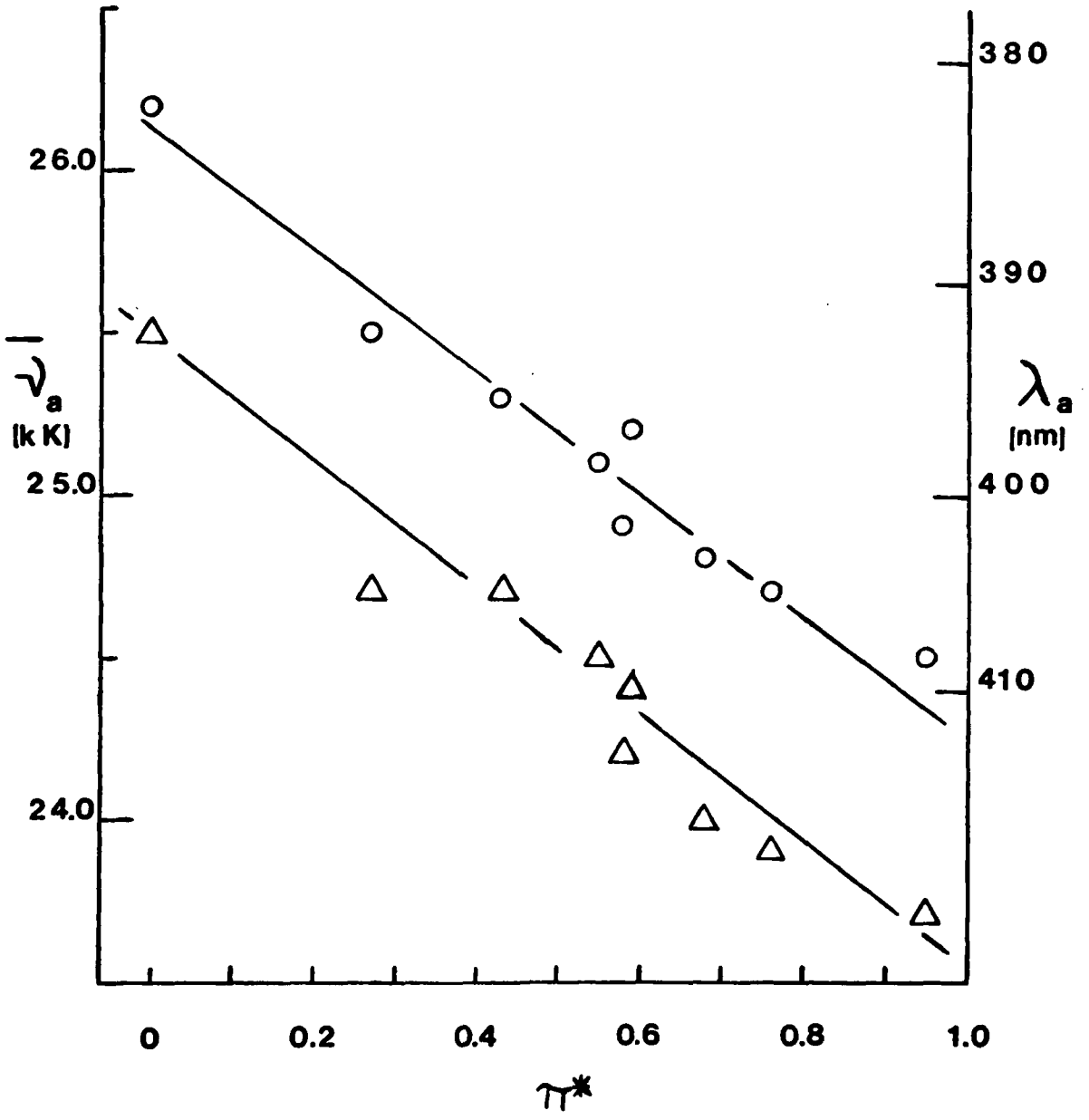


Figure 1. Correlation of absorption frequencies for C6F(Δ) and C8F(o) with the Solvent polarity-polarizability parameter, π*. (Solvents and π* values identified in Table 1)

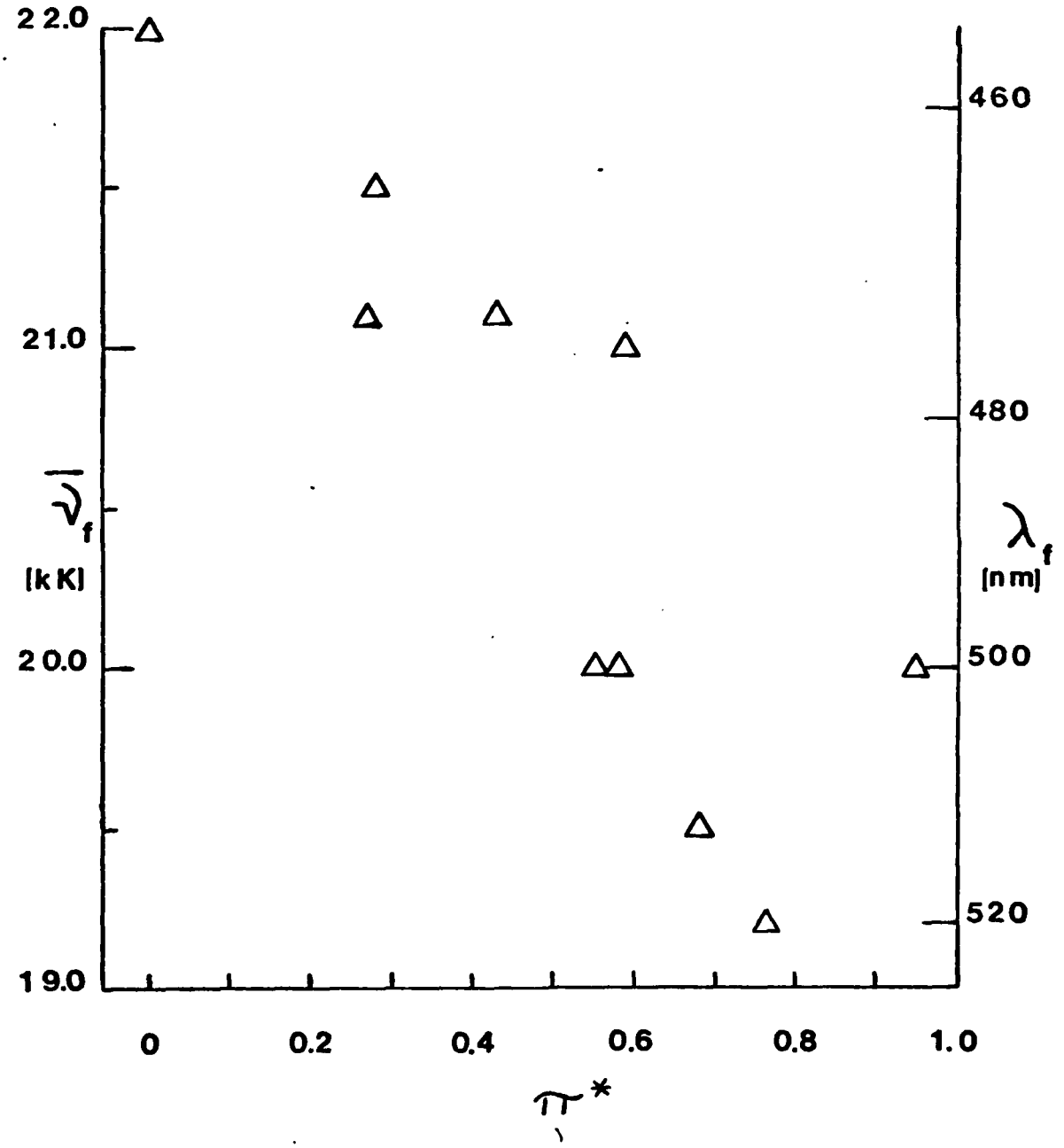


Figure 2. Fluorescence emission frequencies for C6F as a function of the solvent-polarizability parameter, π^*.

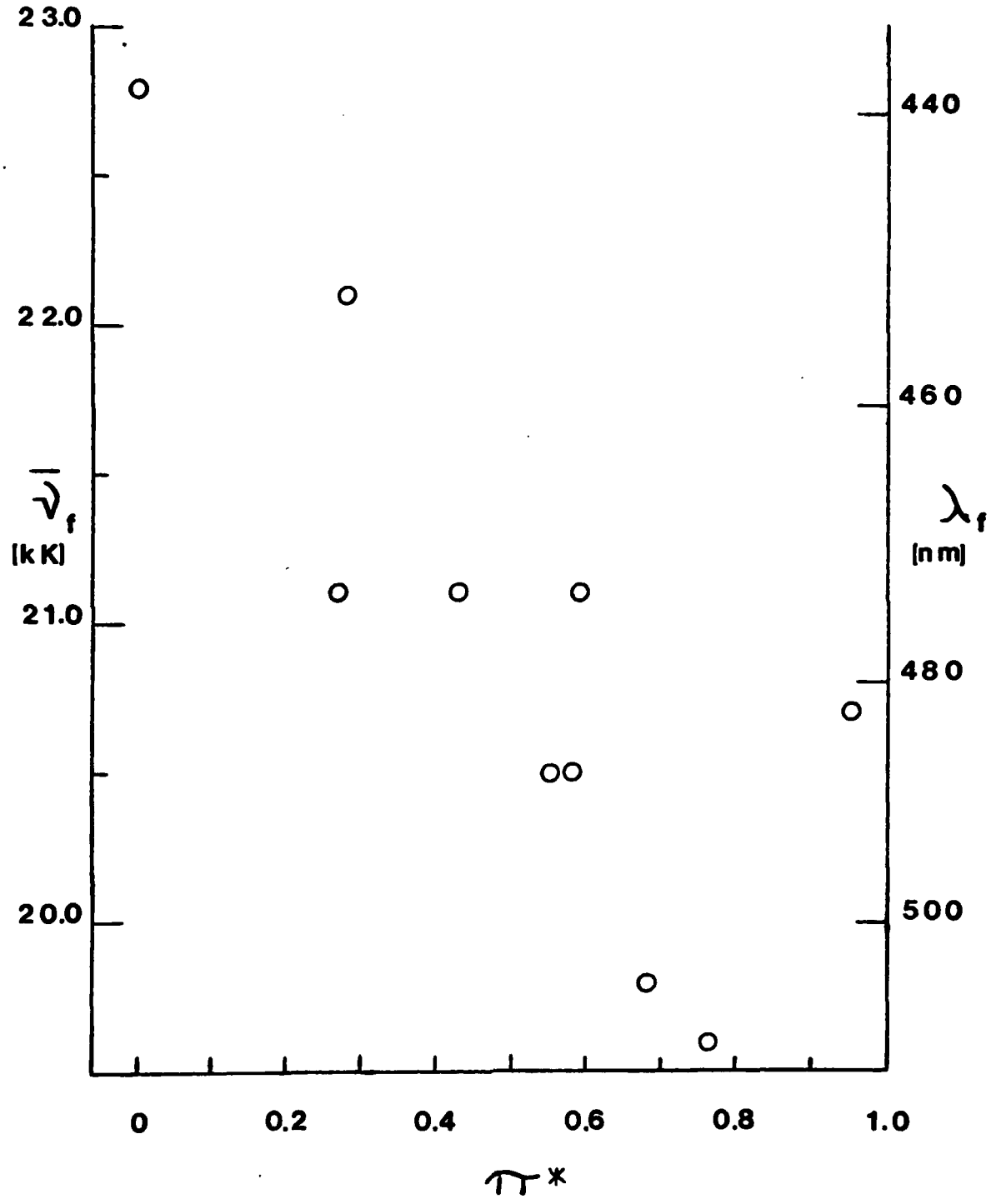


Figure 3. Fluorescence emission frequencies for C8F as a function of the solvent polarity-polarizability parameter, π^*.

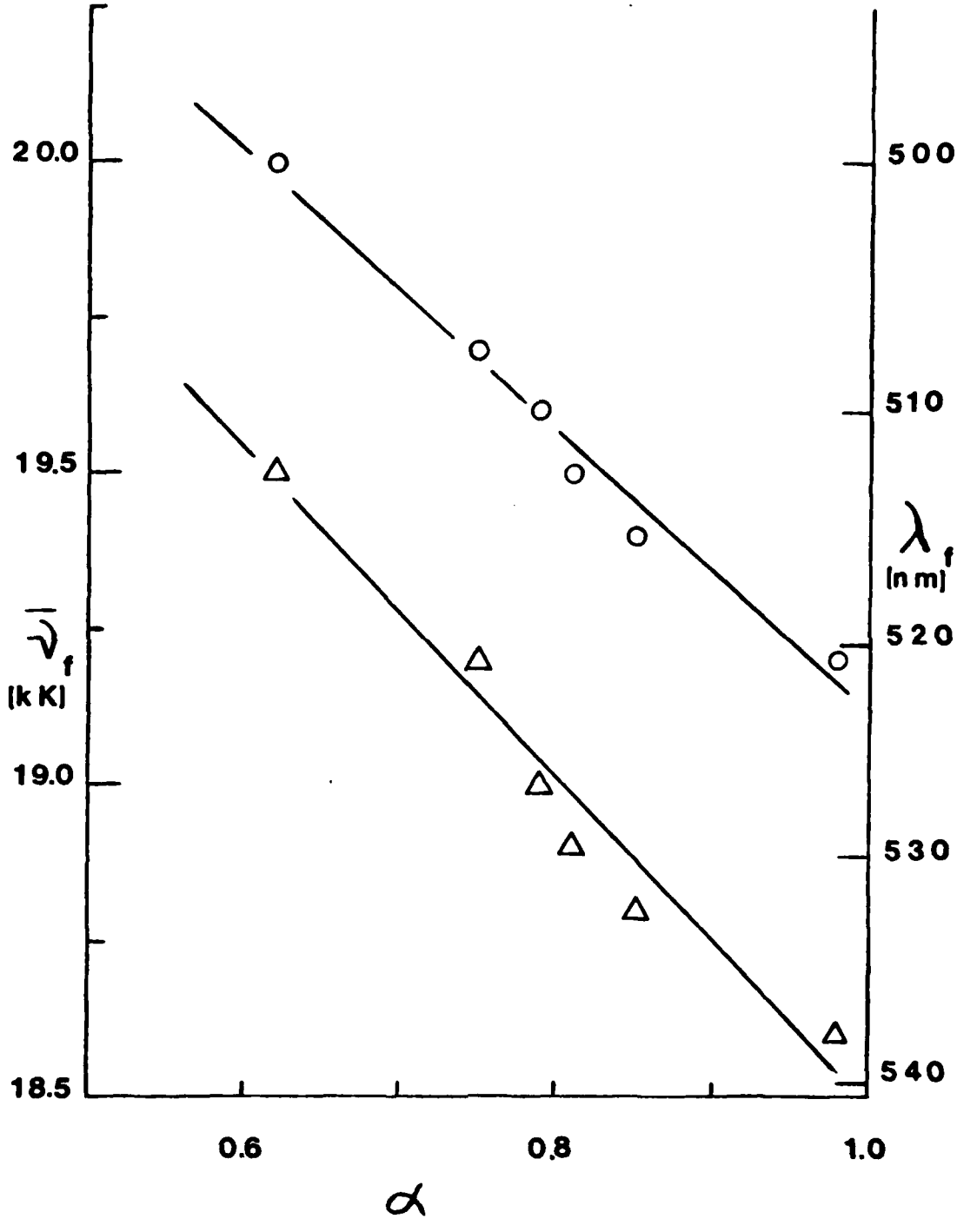
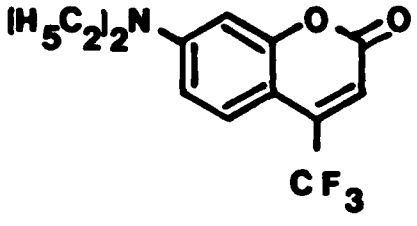
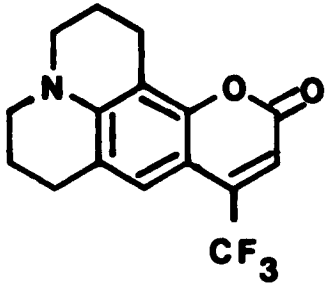


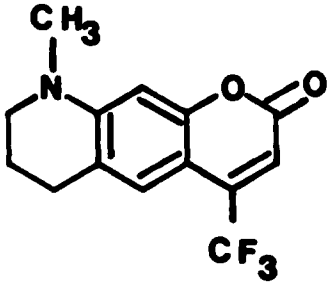
Figure 4. Correlation of fluorescence emission frequencies for C6F (Δ) and C8F (O) with the solvent hydrogen bonding parameter, α.



C1F



C6F



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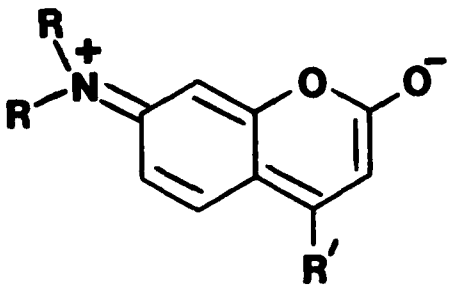

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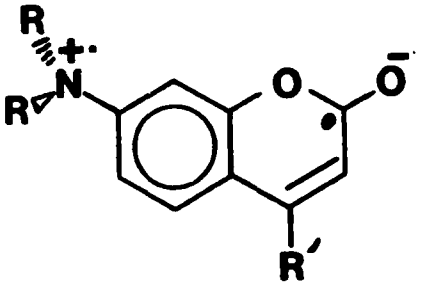

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